

VERIFICATION OF A TRANSLATION

I, the below named translator, hereby declare that:

My name and post office address are as stated below:

That I am knowledgeable in the English language and in the language in which the below identified international application was filed, and that I believe the English translation of the international application No. PCT/JP03/07643 is a true and complete translation of the above identified international application as filed.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.


Date

December 2, 2004

Full name of the translator

Yoshiaki ONISHI

Signature of the translator



Post Office Address

Kitahama TNK Building 7-1, Dosho-machi

1-chome, Chuo-ku, Osaka-shi, Osaka 541-0045,

Japan

-1-

## DESCRIPTION

METALLIC COPPER CATALYST FOR POLYFLUOROALKYLETHYL  
IODIDE PRODUCTION AND PROCESS FOR PRODUCING  
POLYFLUOROALKYLETHYL IODIDE

5

TECHNICAL FIELD

The present invention relates to a process for  
producing a polyfluoroalkylethyl iodide from a  
polyfluoroalkyl iodide and ethylene using a metallic  
10 copper catalyst.

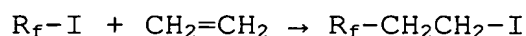
BACKGROUND OF THE INVENTION

Fluorine-containing alkyl iodides have a broad  
range of applications as ingredients for producing a  
15 variety of products such as surfactants, pharmaceuticals,  
functional polymers, etc.

In particular, compounds obtained by an ethylene  
addition reaction between the iodine atom and the  
polyfluoro alkyl group of polyfluoroalkyl iodides (such  
20 compounds are hereinafter referred to as  
polyfluoroalkylethyl iodides) can be converted to various  
other compounds since the iodine therein can be more  
readily substituted by a nucleophile compared with the  
iodine contained in polyfluoroalkyl iodides. Therefore,  
25 polyfluoroalkylethyl iodides have drawn attention as

ingredients for a broad range of products.

As an example of a process for producing such polyfluoroalkylethyl iodides, a process employing an ethylene addition reaction to polyfluoroalkyl iodides (hereinafter simply referred to as an "ethylene addition reaction") as shown below is known:

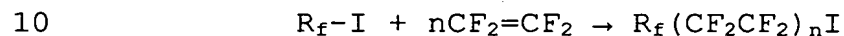


wherein  $R_f$  is a  $C_{1-6}$  polyfluoroalkyl.

In connection with such ethylene addition reactions, processes employing ruthenium/activated carbon (Ru/C), platinum/activated carbon (Pt/C), silver/alumina (Ag/Al<sub>2</sub>O<sub>3</sub>) and like noble metals as catalysts (Konrad von Werner, *Journal of Fluorine Chemistry* 28(1985): 229-233); processes employing azobisisobutyronitrile (AIBN) or benzoyl peroxide and like organic peroxides as catalysts (Neal O. Brace, *Journal of Fluorine Chemistry* 93(1999): 1-25); etc., have been reported. However, noble metals have the disadvantage that they are expensive and thus result in high production costs. Organic peroxides are also expensive and for one-time use only, resulting in high production costs. Furthermore, organic peroxides are disadvantageous in that they are hazardous *per se* and cause inclusion of impurities in the reaction product. Meanwhile, ethylene addition reactions conducted in the presence of metallic copper catalysts have not been

reported.

As an example of a process for producing starting material polyfluoroalkyl iodides, the telomerization reaction conducted in the presence of a copper catalyst as shown below (hereinafter simply referred to as a "telomerization reaction") is known (Japanese Unexamined Patent Publication No. 239336/1996; Qing-Yun Chen, et al., *Journal of Fluorine Chemistry* 36(1987): 483-489; etc.):



wherein  $R_f$  is a  $C_{1-6}$  polyfluoroalkyl and  $n$  is an integer from 1 to 8.

It has not been reported that such a telomerization reaction and the aforementioned ethylene addition reaction can be successively conducted using the same catalyst. If these reactions can be successively conducted in the presence of the same catalyst, simplification of the production process and reduction in production cost are to be expected.

20

#### DISCLOSURE OF THE INVENTION

An object of the present invention is to provide a metallic copper catalyst for use in an ethylene addition reaction to a polyfluoroalkyl iodide and a process for efficiently producing a polyfluoroalkylethyl iodide using

25

such a metal copper catalyst in an ethylene addition reaction to a polyfluoroalkyl iodide.

Another object of the present invention is to provide a process for efficiently producing a  
5 polyfluoroalkylethyl iodide from a polyfluoroalkyl iodide using the same metallic copper catalyst in a telomerization reaction and a subsequent ethylene addition reaction.

Yet another object of the present invention is  
10 to provide a process for efficiently producing a useful polyfluoroalkylethyl acrylate by reacting the polyfluoroalkylethyl iodide obtained according to the aforementioned production process with an acrylic acid salt or the like.

15 The inventors conducted extensive research to solve the problems described above and found a process for producing a polyfluoroalkylethyl iodide employing an ethylene addition reaction in the presence of a metallic copper catalyst. The present invention was accomplished  
20 by conducting further research based on this finding.

In particular, the present invention relates to the following:

Item 1. A metallic copper catalyst for use in an ethylene addition reaction to provide a  
25 polyfluoroalkylethyl iodide from a polyfluoroalkyl iodide

5

•

polyfluoroalkylethyl iodide (IV), the process comprising steps (a) and (b) conducted in the presence of the same metallic copper catalyst:

- (a) a step of reacting tetrafluoroethylene with  
5 a compound represented by Formula (I):



wherein  $R_f$  is a  $C_{1-6}$  polyfluoroalkyl, to produce a compound represented by Formula (III):



- 10 wherein  $n$  is an integer from 1 to 8 and  $R_f$  is as defined above; and

(b) a step of reacting ethylene with compound (III) obtained in step (a) to produce a polyfluoroalkylethyl iodide represented by Formula (IV):



wherein  $R_f$  and  $n$  are as defined above.

- Item 6. A process for producing polyfluoroalkylethyl acrylate (VI), the process comprising steps (a), (b) and (c), steps (a) and (b) being conducted  
20 in the presence of the same metallic copper catalyst:

(a) a step of reacting tetrafluoroethylene with a compound represented by Formula (I):



- wherein  $R_f$  is a  $C_{1-6}$  polyfluoroalkyl, to produce a compound  
25 represented by Formula (III):



wherein n is an integer from 1 to 8 and  $R_f$  is as defined above;

- (b) a step of reacting ethylene with compound  
5 (III) obtained in step (a) to produce a compound represented by Formula (IV):



wherein  $R_f$  and n are as defined above; and

- (c) a step of reacting compound (IV) obtained in  
10 step (b) with a carboxylate represented by Formula (V):

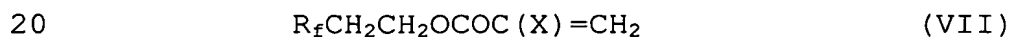


wherein X is H or  $CH_3$  and M is an alkali metal, to produce a polyfluoroalkylethyl acrylate represented by Formula (VI):



wherein  $R_f$ , n and X are as defined above.

Item 7. A process for producing a polyfluoroalkylethyl acrylate represented by Formula (VII):



wherein  $R_f$  is a  $C_{1-6}$  polyfluoroalkyl, and X is H or  $CH_3$ ,

- the process comprising reacting a polyfluoroalkylethyl iodide obtained according to the production process of Item 3 and represented by Formula  
25 (II):





wherein  $R_f$  is as defined above, with a carboxylate represented by Formula (V):



5 wherein X is as defined above, and M is an alkali metal.

The present invention is described in more detail below.

Process for producing polyfluoroalkylethyl iodide (II)

10 A process for producing polyfluoroalkylethyl iodide (II) using the metallic copper catalyst of the present invention is described. This process is for producing a compound represented by Formula (II):



15 wherein  $R_f$  is a  $C_{1-6}$  polyfluoroalkyl, the process comprising reacting ethylene with a compound represented by Formula (I):



20 wherein  $R_f$  is as defined above, in the presence of a metallic copper catalyst.

The metallic copper catalyst of the invention is not limited insofar as it is a copper metal. In view of catalytic activity, the form of the metallic copper catalyst of the invention is preferably powdery, which  
25 ensures a large contact area with the starting materials

on the surface of the metallic copper. The average particle diameter of the powdery copper is, for example, about 0.1 to about 300  $\mu\text{m}$ , and preferably about 30 to about 150  $\mu\text{m}$ .

5           It is sufficient that the metallic copper catalyst is used in an amount of, for example, about 0.1 to about 90 wt.%, preferably about 0.5 to about 10 wt.%, based on the weight of compound (I).

          Moreover, the metallic copper catalyst of the  
10 present invention may be a catalyst in which metallic copper is supported on a carrier. Usable carriers are not limited insofar as the activity of the metallic copper catalyst is not adversely affected, and examples thereof include metal oxides. Specific examples are single-metal  
15 oxides selected from the group consisting of zinc oxide, iron oxide, copper oxide, titanium oxide, zirconium oxide, cerium oxide, aluminum oxide and silicon oxide; complex oxides comprising 2 or more metal elements selected from the group consisting of zinc, iron, copper, titanium,  
20 zirconium, cerium, aluminum and silicon; etc. Although the form of carrier supporting the metallic copper catalyst is not limited, it is preferably powdery in view of catalytic activity. The metallic copper can be supported on the carrier according to known methods.

25           The amount of metallic copper in a metallic

copper catalyst wherein the metallic copper is supported on a carrier is about 0.01 to about 50 wt.%, preferably about 0.1 to about 20 wt.%, based on the total amount of catalyst.

5           A metallic copper catalyst in which metallic copper is supported on a carrier is used in an amount of, for example, about 0.1 to about 90 wt.%, preferably about 0.5 to about 10 wt.%, based on the weight of compound (I).

Other metals may be used with the metallic  
10 copper catalyst of the present invention to enhance its catalytic activity. Examples thereof include titanium, chromium, iron, cobalt, nickel, tin, etc. Among such other metals, tin is preferable. Such other metals are used in an amount of, for example, about 0.1 to about 90  
15 wt.% relative to the weight of the metallic copper catalyst, and preferably about 10 to about 30 wt.%. They are preferably powdery in view of catalytic activity.

Examples of polyfluoroalkyls represented by  $R_f$  include  $C_{1-6}$  linear or branched perfluoroalkyls and alkyls  
20 wherein at least one hydrogen atom contained in  $C_{1-6}$  linear or branched alkyls are substituted with fluorine. Specific examples are  $CF_3$ ,  $C_2F_5$ ,  $n-C_3F_7$ ,  $i-C_3F_7$ ,  $n-C_4F_9$ ,  $i-C_4F_9$ ,  $sec-C_4F_9$ ,  $tert-C_4F_9$ ,  $n-C_5F_{11}$ ,  $i-C_5F_{11}$ ,  $n-C_6F_{13}$ ,  $i-C_6F_{13}$  and like perfluoroalkyls; and  $CHF_2(CF_2)_m$  ( $m$  is an integer  
25 from 1 to 5),  $CH_2F(CF_2)_m$  ( $m$  is an integer from 1 to 5) and

like alkyls wherein fluorine atom(s) substitute hydrogen atom(s) contained in the alkyl group. These compounds may be prepared according to known methods.

Compound (I) may be reacted with ethylene gas  
5 under pressure in the presence of the metallic copper catalyst. The ethylene gas pressure is, for example, about 0.01 to about 3 MPa, and preferably about 0.1 to about 1 MPa. Ethylene gas is used in an amount of, for example, about 1 to about 1.2 mol per mol of Compound (I).

10 The reaction can be conducted by, for example, introducing compound (I) and the metallic copper catalyst into an autoclave or like a reactor for pressurizing and heating; deaerating the reactor; raising the temperature by a heater to the reaction temperature; introducing  
15 ethylene gas into the reactor; and stirring at that temperature for a specific period of time. The reaction temperature is, for example, about 50 to about 200°C, preferably about 70 to 120°C, in view of safety and reaction speed. In this reaction, as ethylene is consumed,  
20 the pressure in the reactor decreases. It is preferable to keep the pressure constant by supplying ethylene as and when necessary because low pressures in the reactor result in slow reaction speeds. In this reaction, the end point is determined to be when no ethylene pressure decrease is  
25 observed. Although the reaction time varies depending on

the reaction conditions, it is usually about 0.5 to about 4 hours.

The reaction is afforded a high conversion rate by the use of the aforementioned metallic copper catalyst.

5 Moreover, it gives a monoethylene adduct with a high selectivity. Furthermore, since the aforementioned metallic copper catalyst is a solid catalyst, it has the advantage that it can be readily separated from the reaction product and reused.

10

Process for producing polyfluoroalkylethyl iodide (IV)

Next, described is a process for producing polyfluoroalkylethyl iodide (IV) employing a telomerization reaction and an ethylene addition reaction,  
15 both of which are conducted in the presence of the metallic copper catalyst of the present invention.

The telomerization reaction refers to a reaction to produce a compound represented by Formula (III):



20 wherein n is an integer from 1 to 8 and  $R_f$  is a  $C_{1-6}$  polyfluoroalkyl, by reacting tetrafluoroethylene with a compound represented by Formula (I):



wherein  $R_f$  is as defined above.

25 Specific examples of polyfluoroalkyls

represented by  $R_f$  contained in starting compound (I) are as described above.

5       Metallic copper catalysts usable are those described in relation to the ethylene addition reaction above.

10       The reaction may be conducted according to known methods. The reaction may be carried out by, for example, introducing compound (I) and the metallic copper catalyst into an autoclave or like a reactor for heating and  
15       pressuring; deaerating the reactor; raising the temperature by a heater to about 80 to about 140°C; introducing tetrafluoroethylene gas into the reactor; maintaining the pressure in the reactor at about 0.3 to about 1.2 MPa; and stirring at that temperature and  
15       pressure for a specific period of time.

20       After the telomerization reaction, the telomeric reaction product may be successively subjected to the aforementioned ethylene addition reaction in the same reactor without isolation. The metallic copper catalyst  
25       used in the telomerization reaction can be used as it is in the following ethylene addition reaction. When the ethylene addition reaction is successively performed after the telomerization reaction, it is preferable to remove tetrafluoroethylene and deaerate the reactor before the  
25       ethylene addition reaction.

Alternatively, after the telomerization reaction, the telomeric reaction product may be isolated and then subjected to the following ethylene addition reaction. In this case, telomers with a low polymerization degree (e.g., those having 6 or fewer carbons atoms) are preferably separated by distillation for recycling.

Using the production process comprising a series of steps of the present invention, compound (IV) can be efficiently produced from compound (I) in one sequence.

10

Process for producing polyfluoroalkylethyl acrylate (VI)  
or (VII)

Described here is a process for producing polyfluoroalkylethyl acrylate (VI) or (VII), which is used as an ingredient for, e.g., water- and oil-repelling polymers, after the telomerization and ethylene addition reactions using the metallic copper catalyst of the invention.

This process refers to a process for producing a compound represented by Formula (VI):



wherein  $R_f$  and  $n$  are as defined above and  $X$  is H or  $CH_3$ , by reacting a carboxylate represented by Formula (V):



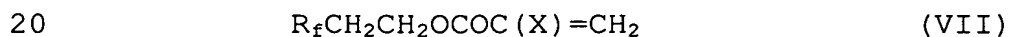
wherein  $X$  is as defined above and  $M$  is an alkali metal,

with compound (IV) obtained according to the  
aforementioned telomerization and ethylene addition  
reactions.

The reaction between compound (IV) and  
5 carboxylate (V) may be carried out by, for example, mixing  
compound (IV) with carboxylate (V) in an alcoholic solvent  
(e.g., amyl alcohol, *t*-butanol, 2-propanol or the like)  
under ordinary pressure, heating while stirring at usually  
about 150 to about 200°C for about 4 to about 12 hours,  
10 and separating polyfluoroalkylethyl acrylate (VI) from the  
reaction mixture.

Examples of alkali metals represented by M  
include sodium, potassium, etc. Among these, potassium is  
preferable in view of reactivity.

15 Meanwhile, by reacting polyfluoroalkylethyl  
iodide (II) obtained by the previously-mentioned  
production process with carboxylate (V) under the  
conditions described above, another polyfluoroalkylethyl  
acrylate represented by Formula (VII):



wherein  $R_f$ ,  $n$  and  $X$  are as defined above can be prepared.

Using the production process comprising a series  
of steps of the present invention, compound (VI) or (VII),  
both of which are useful as ingredients for water- and  
25 oil-repelling polymers, can be efficiently produced from



compound (I).

BEST MODE FOR CARRYING OUT THE INVENTION

Examples are given below to illustrate the invention in more detail, but the scope of the invention is not limited to these examples.

Example 1 (Ethylene addition reaction)

Into a 200 ml Hastelloy (registered trademark) autoclave were introduced 138.6 g of perfluoroethyl iodide ( $\text{CF}_3\text{CF}_2\text{I}$ ) and 8.21 g of copper powder (average particle diameter: 45  $\mu\text{m}$ , manufactured by Mitsui Mining & Smelting Co., Ltd.). The autoclave was deaerated, and the temperature was raised to 80°C. Ethylene was charged into the autoclave to an inner pressure of 1.0 MPa. As the perfluoroethyl iodide is consumed, the pressure in the autoclave is decreased and the partial pressure of the ethylene is increased. Therefore, to maintain the aforementioned pressure, ethylene was charged while monitoring the pressure. The time at which no ethylene pressure decrease was observed was determined as the end point of the reaction. The reaction time was 80 minutes. After cooling the reaction mixture, the reaction product was analyzed by gas chromatography (GC).

The conversion of the perfluoroethyl iodide was 99.5%, and the selectivity for the resulting ethylene

adduct (adduct of one ethylene molecule) was 99.8%.

(GC Conditions)

Column: SE-30 3 m

5 Detector: TCD 100 mA

Carrier gas: helium 50 ml/min

Temperature of the inlet (injection port) and the  
detector: 250°C

Conditions for temperature increase: 50°C (no retention) →  
10 10°C/min → 250°C (10-minute retention)

Column: Pora-Q 3 m

Detector: TCD 100 mA

Carrier gas: helium 50 ml/min

Temperature of the inlet (injection port) and the  
15 detector: 250°C

Conditions for temperature increase: 50°C (no retention) →  
20°C/min → 250°C (10-minute retention)

When a polyfluoroalkyl iodide having 1-4 carbon  
atoms was used as a starting material, the Pora-Q column  
20 was used. When a polyfluoroalkyl iodide having at least 5  
carbon atoms was used as a starting material, the SE-30  
column was used.

Examples 2-6 (Ethylene addition reaction)

25 Reactions were conducted in the same manner as

in Example 1 except that the perfluoroethyl iodide was replaced with 1-iodoperfluorooctane ( $n\text{-C}_8\text{F}_{17}\text{I}$ ).

After cooling the reaction mixtures, the reaction products were analyzed by gas chromatography (GC).

5 Table 1 shows the results.

Comparative Example 1 (Ethylene addition reaction)

A reaction was conducted in the same manner as in Example 1 except that the perfluoroethyl iodide and the  
10 copper catalyst were replaced with 1-iodoperfluorooctane ( $n\text{-C}_8\text{F}_{17}\text{I}$ ) and an organic peroxide, i.e., *t*-butylperoxyisopropyl monocarbonate (Perbutyl I, manufactured by NOF Corporation), respectively.

After cooling the reaction mixture, the reaction  
15 product was analyzed by gas chromatography (GC). Table 1 shows the results.

Table 1

	n-C <sub>8</sub> F <sub>17</sub> I g	Copper catalyst g (wt.% *)	Reaction temperature °C	Ethylene pressure MPa	Reaction time Min	Conversion GC %
Ex. 2	132	13.4 (10)	80	0.1	105	99.94
Ex. 3	130.8	2.66 (2)	80	0.1	120	99.71
Ex. 4	125.3	2.51 (2)	80	0.55	58	99.89
Ex. 5	155.2	3.11 (2)	120	0.1	56	99.97
Ex. 6	122.5	0.62 (0.5)	120	0.55	40	99.86
Comp. Ex. 1	133.2	0.13 **	105	0.1-0.2	180	97.7

\*: wt.% relative to n-C<sub>8</sub>F<sub>17</sub>I

\*\*: conducted using *t*-butylperoxyisopropyl monocarbonate (Perbutyl I) as a catalyst

5

The conversion of each 1-iodoperfluorooctane of Examples 2-6 was more than 99.7%. The selectivity for the resulting ethylene adduct (adduct of one ethylene molecule) was 99.9% or greater in each case.

10

Example 7 (Telomerization reaction - ethylene addition reaction)

(1) Into a stirred tank pressure reactor equipped with a stirrer were introduced 100 g of 1-iodoperfluorobutane (n-C<sub>4</sub>F<sub>9</sub>I) and 4 g of copper powder (325 mesh, manufactured by Kishida Chemical Co., Ltd.), and the reactor was then heated to 110°C. Tetrafluoroethylene was introduced into the reactor at that temperature, and the pressure in the reactor was increased to 0.38 MPa.

15

Tetrafluoroethylene is consumed as the reaction progresses. Therefore, to maintain the pressure at the aforementioned level, tetrafluoroethylene was supplied as and when necessary while monitoring the reactor pressure. After  
5 introducing tetrafluoroethylene to a total of 18 g, the reaction was stopped.

A sample was collected from the reaction mixture in the reactor to analyze the product by gas chromatography (GC). Table 2 shows the results. The conversion was 40.0%.  
10

Table 2

Reaction product distribution: $\text{CF}_3\text{CF}_2\text{CF}_2\text{CF}_2(\text{CF}_2\text{CF}_2)_n\text{I}$						
n	0	1	2	3	4	5
mol%	60.0	34.5	5.1	0.63	0.072	0.009

(2) The reactor was deaerated, and the temperature thereof was increased to 80°C. Ethylene was  
15 slowly charged into the reactor to an inner pressure of 0.8 MPa. The procedures described in Example 1 were then repeated.

The conversion of the perfluoroethyl iodide was 99.8%, and the selectivity for the resulting ethylene  
20 adduct (adduct of one ethylene molecule) was 100%.

#### INDUSTRIAL APPLICABILITY

According to the production process of the

present invention, a polyfluoroalkylethyl iodide can be efficiently produced from a polyfluoroalkyl iodide employing an ethylene addition reaction conducted in the presence of an inexpensive metallic copper catalyst. The  
5 use of a metallic copper catalyst allows a low reaction temperature, enabling the catalyst after reaction to be readily separated and reused.

Furthermore, according to the production process of the present invention, since a telomerization reaction  
10 and an ethylene addition reaction can be conducted in one sequence using the same metallic copper catalyst, the series of steps for polyfluoroalkylethyl iodide production can be simplified, and the production cost can be reduced accordingly.